

Title: Development of Fundamental Data on Chemical Speciation and Solubility for Strontium and Americium in High Level Waste: Predictive Modeling of Phase Partitioning during Tank Processing.

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Research Objective

In this research program, Pacific Northwest National Laboratory (PNNL) and Florida State University (FSU) are investigating the speciation of Sr and Am/Cm in the presence of selected organic chelating agents (ethylenediaminetetraacetic acid (EDTA), N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), nitrilotriacetic acid (NTA), and iminodiacetic acid (IDA)) over ranges of hydroxide, carbonate, ionic strength, and competing metal ion concentrations present in high level waste tanks. The project is comprised of integrated research tasks that approach the problem of chemical speciation using macroscopic thermodynamic measurements of metal-ligand competition reactions, molecular modeling studies to identify structures or complexes of unusual stability, and mass spectrometry measurements of complex charge/mass ratio that can be applied to mixed metal-chelate systems. This fundamental information is then used to develop thermodynamic models which allows the prediction of changes in chemical speciation and solubility which can occur in response to changes in tank processing conditions. In this way we can both develop new approaches that address fundamental problems in aqueous speciation and at the same time provide useful and practical information needed for tank processing.

Problem Statement

Current strategies for reducing the total volume of radioactive tank waste requiring disposal at Hanford and other DOE sites call for the development of methods to selectively dissolve and remove non-radioactive elements such as Al, P, and Cr while retaining or precipitating the radioactive elements, including Sr and the actinide elements, in the tank sludges. This partitioning between solids and precipitates is fundamentally dependent upon the chemical speciation of the elements present in the tank processing solutions. Of particular importance is separation of the radioactive and hazardous actinide elements and fission products from the sludges and supernatants, particularly from supernatants containing high concentrations of strong chelating agents which can act to solubilize the actinides and fission products as well as interfere with subsequent metal ion extraction processes. Specifically, the fundamental understanding of chemical speciation reactions gained from these studies is needed to propose methodologies for removal of Sr and Am/Cm from organic chelates present in high level tank waste, via competition, displacement or other reactions, without the need for the development of costly and potentially hazardous organic destruction technologies.

Research Accomplishments:

Beginning in October 1996, we initiated a research program on Sr and trivalent actinide speciation in these high ionic strength, strongly basic solutions in the presence of organic chelates and competing metal ions. These data on chemical speciation and solubility were then used to develop aqueous thermodynamic models, based upon the Pitzer equations, for describing the chemical behavior of these elements in high ionic strength electrolytes.

The studies proceeded in a systematic manner beginning with the effects of hydrolysis (hydroxide concentration) on the chemical speciation of Sr to high base concentration. This was followed by studies on the effects of carbonate complexation on Sr extending to high carbonate concentration. This completed the studies of the major inorganic complexants for Sr and formed the foundation for the organic chelate studies. Studies on the effects of the organic chelates EDTA, HEDTA, NTA, and IDA were then completed. The effects of only one competing metal, Ca, were studied. The studies on Ca also required studying the effects of hydrolysis and carbonate complexation on the speciation and solubility of Ca since these factors must also be known to unravel the effects of a competing metal ion. Following the completion of the studies on Sr, the studies on the trivalent actinide analog, Eu(III) were conducted. These studies included the effects of high base on the complexation of EDTA, HEDTA, NTA, and IDA. These studies were completed in 1999. No studies on the effects of competing metal ions on the speciation of the trivalent actinides were conducted. The following section gives a brief summary of much of this work.

Studies on Sr speciation

In order to unravel the speciation reactions of Sr in complex tank waste requires studies of speciation reactions in the presence and absence of chelators. Specifically, in these initial studies speciation reactions in four chemical systems: Na-Sr-OH-H₂O, Na-Sr-CO₃-H₂O, Na-Ca-OH-H₂O, and Na-Ca-CO₃-H₂O with and without added chelators were studied. The systems including Ca as well as Sr were studied because of the presence of large amounts of Ca in tanks waste and high affinity of Ca²⁺ for the organic chelators.

This combined experimental and modeling approach also resulted in an aqueous thermodynamic model for the Na-Ca-Sr-OH-CO₃-H₂O system valid to high concentration at 25⁰C. The first published values of the equilibrium constants for the formation of Sr(CO₃)₂²⁻, and Ca(CO₃)₂²⁻ aqueous species and of the solubility product of Sr(OH)₂·8H₂O were determined along with the necessary Pitzer ion-interaction parameters to model these chemical systems. In the development of these thermodynamic model, computational chemistry methods were used to provide unique insight into the aqueous speciation reactions. The molecular modeling results were used to help determine whether ion-interaction or ion pairing approaches were appropriate in the thermodynamic analysis, suggested the possible existence of higher carbonate complexes in solution, and provided at least some guidance as to the reasonableness of independently calculated equilibrium constants.

Following these studies, the effects of calcium, hydroxide, and carbonate on the displacement of Sr from four organic chelates: EDTA, HEDTA, NTA, and IDA were studied in solutions with high base and carbonate concentration. Increases in hydroxide were ineffective in removal of Sr from the chelators even at base concentrations as high as 6M. Increases in carbonate concentration were effective in displacing Sr from the weaker chelators IDA and NTA but not from the strongest chelators HEDTA and EDTA. Competition with other metal ions, in this case Ca under highly basic and carbonate conditions, was shown to effectively displace Sr from the strong chelating agents

HEDTA and EDTA, depending upon the concentration of Sr and the competing metal ions. Further, under a wide range of conditions, predominant chemical equilibrium constraints, were identified that resulted in simple predictive models for aqueous Sr and Ca organic-chelate complexes which are independent of the ionic media and thus can be applied to conditions with widely varying electrolyte composition.

An example of the effect of metal ion displacement of Sr by Ca is given in Figure 1 for the CaCO_3 - SrCO_3 -EDTA system. In the absence of Ca, the added EDTA stoichiometrically complexes with Sr and solubilizes the solid strontianite. Upon the addition of Ca (as calcite) the strong affinity of Ca for EDTA results in stoichiometric complexation of the EDTA with Ca and effective displacement of Sr from the EDTA into the solid strontianite. This effect reduces the solubility of Sr in these solutions by almost three orders of magnitude. Clearly, such metal ion displacement reactions must be well understood to predict the effects of the chelators on Sr complexation. This result also indicates that metal ion displacement, if properly understood and manipulated, may represent an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank processing, especially given the fact that the strongest chelators represent only a small fraction of the total organic carbon in tank waste (see Table 1).

The results of these studies have been published in the open literature and presented at national society meetings and conferences (Oakes et al. 2000; Felmy and Mason 1998; Felmy et al. 1998; Felmy et al. 1997a,b,c; Sterner et al. 1998).

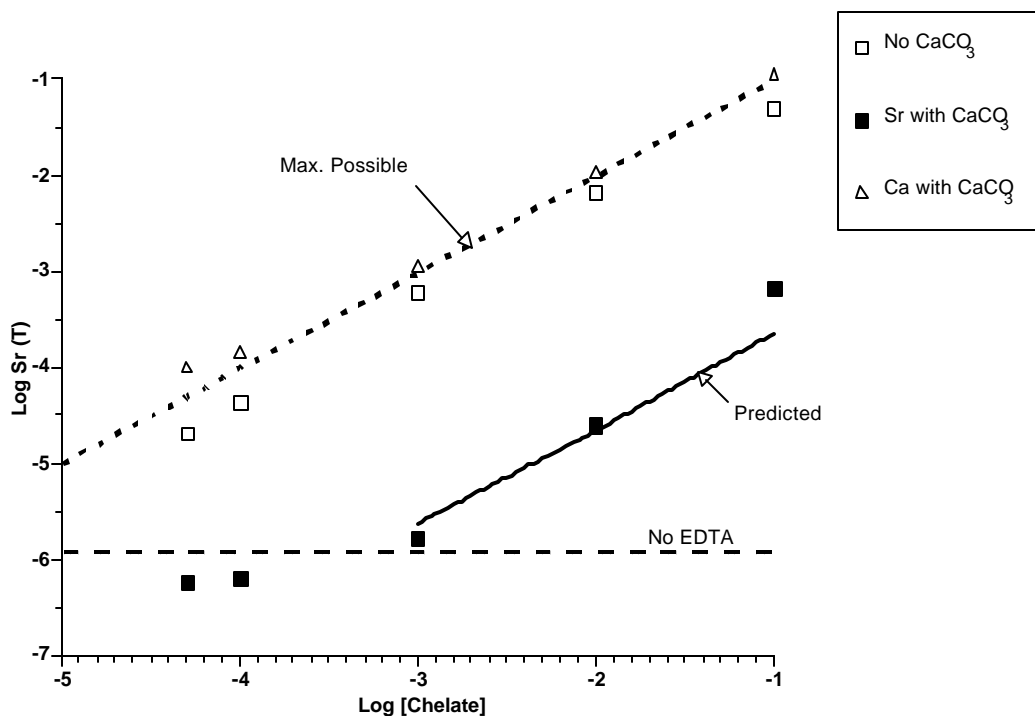


Figure 1. The solubility of $\text{SrCO}_3(\text{c})$ with added $\text{CaCO}_3(\text{c})$ in $0.1\text{m Na}_2\text{CO}_3$. Solid lines represent model predictions.

Trivalent Actinide Studies

Studies on the solubility of Eu (III), a trivalent actinide analog, compounds [i.e. $\text{Eu}(\text{OH})_3(\text{c})$] were then completed as a function of base concentration in the presence of four organic chelates: EDTA, HEDTA, NTA, and IDA. $\text{Eu}(\text{OH})_3(\text{c})$ was chosen for study owing to its very low solubility under high base concentration. These studies have shown that high base concentration can displace Eu(III) from all of the organic chelates studied. The effective NaOH concentration for the displacement reaction being dependent on the nature of the specific chelate studied and the chelate concentration.

Thermodynamic analysis of these experimental data, coupled with Time Resolved Laser Luminescence Spectroscopy (TRLFS) studies of the species in solution, indicated that formation of mixed metal-chelate-hydroxide complexes is occurring in solution. These mixed metal-chelate-hydroxide complexes increase the effectiveness of the chelates in solubilizing Eu(III) under high base conditions. The number of hydroxide ions bound to the metal-ligand complex varies with the chelate type. The structural and energetic reasons for this variability in solution coorelate with density functional theory (DFT) calculations for gas phase La(III) clusters. In the case of EDTA and HEDTA, solution complexes form with either one or two hydroxyl ions associated with the metal-chelate complex (i.e. $\text{Eu}(\text{OH})\text{EDTA}^{2-}$, $\text{Eu}(\text{OH})\text{HEDTA}^-$, and $\text{Eu}(\text{OH})_2\text{HEDTA}^{2-}$) whereas in the case of NTA there is at most only one hydroxyl associated with the metal-chelate complex (e.g. EuOHNTA^- or $\text{EuOH}(\text{NTA})_2^{4-}$). The first determination of the stability constants for three of these species ($\text{Eu}(\text{OH})\text{EDTA}^{2-}$, $\text{Eu}(\text{OH})_2\text{HEDTA}^{2-}$, and $\text{EuOH}(\text{NTA})_2^{4-}$) as well as for the $\text{Eu}(\text{OH})_4^-$ species were determined. An aqueous thermodynamic model is presented which describes all of the available thermodynamic data for these chemical systems, to high ionic strength, and correlates with the DFT calculations.

The effects of these mixed metal-chelate-hydroxyl complexes is illustrated in Figure 2 for the solubility of $\text{Eu}(\text{OH})_3(\text{c})$ in EDTA solutions with added base. The formation of the mixed Eu-EDTA-OH complexes (specifically EuOHEDTA^{2-}) increases the solubility by orders of magnitude over the results in the absence of EDTA. Interestingly, the currently available thermodynamic models, which only include a EuEDTA^- species, underpredict the observed solubilities by two to three orders of magnitude depending upon the hydroxide concentration. Clearly, predicting the effects of such speciation reactions is critical to understanding the solubility and aqueous thermodynamics of the trivalent actinides in chelate containing solutions under basic conditions.

These results have been presented at society meetings (Felmy et al. 1999; Felmy and Mason 1998) and the manuscripts have been published (Felmy and Rai 1999) or in press (Felmy et al. 2000).

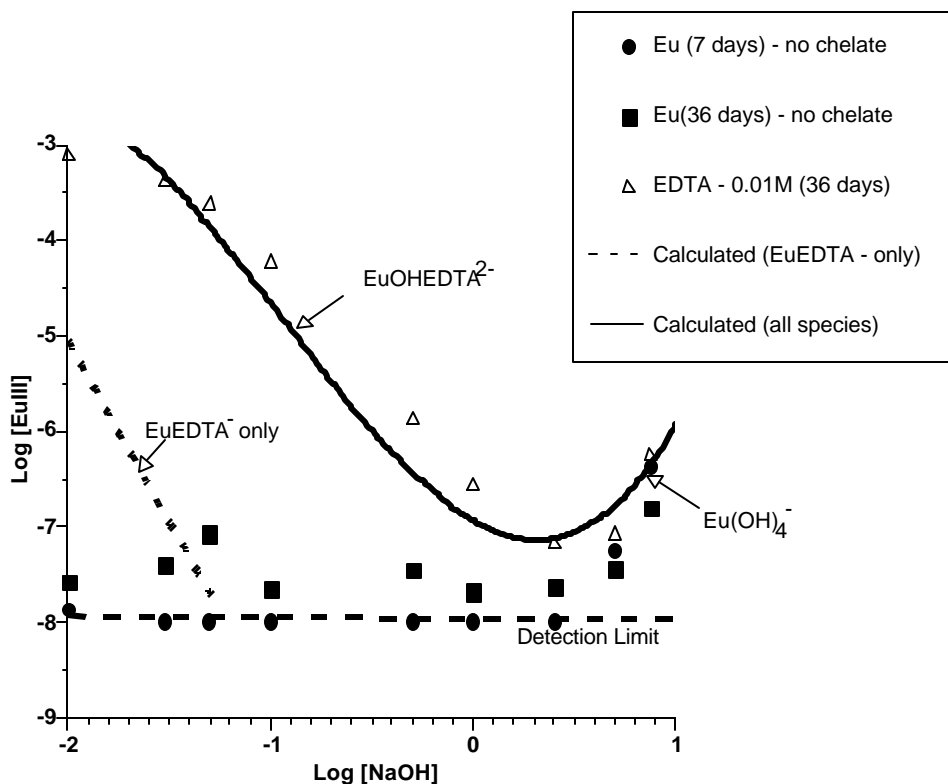


Figure 2. The solubility of $\text{Eu}(\text{OH})_3(\text{c})$ in NaOH in the presence and absence of 0.01m EDTA. Dashed line represents the model predictions before this study and without the EuOHEDTA^{2-} species included. Solid line represents our current model predictions.

Implications for Waste Tank Processing

Sr Studies

These results have some interesting implications as regards processing basic/carbonate solutions such as those in high level tank waste. First, given the expected range in chelate concentrations present in tank waste and the fact that carbonate is present in significant concentration in all tanks, it is likely that the chemical speciation of Sr will be almost certainly unaffected by the presence of IDA and probably also unaffected by the NTA as well. Only HEDTA and EDTA appear to be present at high enough concentration and form strong enough complexes to significantly impact the speciation of Sr in tank waste. Such results are important in limiting the number of chemical species that need to be considered in chemical modeling of tank processing strategies. In addition, competition with other metal ions present in such solutions, in this case Ca, can effectively displace Sr from the strong chelating agents HEDTA and EDTA, depending upon the concentration of Sr and the competing metal ions. This result indicates that metal ion displacement may represent an acceptable alternative to costly and hazardous organic destruction technologies in reducing the impacts of organic chelates in tank

processing, especially given the fact that the chelators represent only a small fraction of the total organic carbon in tank waste. In a more general sense, these results also have direct implications to chemical processing applications under high base conditions where the build up of scale forming minerals (e.g. CaCO_3), can effect the removal of other metal ions by organic chelators.

Trivalent Actinides

The presence of the mixed metal-chelate-hydroxyl species can significantly impact waste tank processing strategies designed to either keep the trivalent actinides in the waste sludges or separate the actinides from the tank supernate. The solubility data themselves reveal that at chelate concentrations typical of tank solutions (i.e. $\sim 0.01\text{M}$) that basic solutions of 5M NaOH are required to remove the trivalent actinides from solution. This contrasts sharply with current model predictions that indicate that such removal should occur closer to 0.1M NaOH . The thermodynamic data developed here can be used in a wide range of applications including: evaluating the effects of competing metal ions on ligand displacement and solubility, evaluating the effects of waste mixing strategies from tank to tank, and determining the chemical forms and stability of complexes that can effect separation processes such as solvent extraction or ion exchange. Thermodynamic models capable of using these results are currently being used at Hanford and other sites. Finally, it should be noted that a significant fraction of the organic carbon present in tank waste (23-61%) is comprised of low molecular weight organic acids, such as acetate, glycolate, and formate. The results of this study for IDA indicate that even relatively strong ligands ($\text{Log } K \sim 7$) will not be able to solubilize trivalent actinides under basic conditions. Therefore, since most of the low molecular weight organic acids have relatively low binding constants with the trivalent actinides ($\text{Log } K \sim 2-3$) these ligands will probably not have much effect on tank processing strategies. Accurate thermodynamic models for these species are therefore not required.

In addition, the thermodynamic models developed as part of this study are currently being used by the Hanford private contractor (BNFL) to design better waste separation processes for Sr and the trivalent actinides.

Additional Research Needs

In order to extend these results to a wider range of waste tank compositions requires additional research in three areas: 1) extension to important chelates not previously studied, 2) studies of competing metal ions, and 3) specific studies using Am(III)/Cm(III) . The chelate complex studies are needed to extend our previous research on EDTA, HEDTA, NTA, and IDA to citrate and oxalate. Mixed ligand-ligand complexation effects should also be addressed for Eu(III) in EDTA-HEDTA, EDTA-NTA, and HEDTA-NTA solutions to high base concentration. Studies of competing metals should include those metals (i.e. Ni, Al, Mn, and Fe) which are present in highest concentration in the waste tanks. These fundamental data on chemical speciation and solubility will then be used to develop highly accurate thermodynamic models valid to

high ionic strength. Such information will allow the analysis and modeling of a much wider range of tank waste compositions.

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